

# PATENT SPECIFICATION

(11) 1 350 225

1 350 225

- (21) Application No. 55325/71 (22) Filed 29 Nov. 1971  
 (31) Convention Application No. 93839 (32) Filed 30 Nov. 1970 in  
 (33) United States of America (US)  
 (44) Complete Specification published 18 April 1974  
 (51) International Classification C08G 5/00; C14C 3/18; D06M 15/46 //  
 C14C 3/06, 3/28, 9/02



- (52) Index at acceptance  
 C3R 1D1A1 1D1A2 1D1AX 1D1X 1D2A 1D2BX 1D2C  
 1D2D 1D2E 1D2F 1E2B 1E6 1N1H 1N1X  
 1N2QX 1N4  
 C6C 2A1 2B 2J2 2L3B 2L6  
 D1P 260 26Y 361 365 36Y 370 382 390 391 39Y 490  
 49Y 505 50Y 560 562 563 566 568 56Y 605  
 612 655 65Y 69Y L6

## (54) IMPROVEMENTS IN OR RELATING TO LEATHER

(71) We, DIAMOND SHAMROCK CORPORATION, of 300 Union Commerce Building, Cleveland, Ohio 44115, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for leather treating and processes for their use.

Chrome and/or mineral tanned leathers are at present retanned with syntans, vegetable extracts and/or resins of various types. This is done to impart retan effects or characteristics which chrome and/or mineral tanned leather does not of itself possess. The effects or characteristics include: bleaching, dye assisting, plumping, increased weight, less shrinkage, better feel, better grain character, and buffability. Conventional retan material generally imparts to chrome and/or mineral tanned leather a positive characteristic of rewetting and water absorption. Conventional leather lubricants applied as emulsions (fatliquors) generally add to this characteristic of wetting. Various materials such: hydrophobic rubbers and resins, fluorocarbons, fatty chrome complexes, silicones, and waxes, are applied on top of conventional retan and fatliquor treatments to overcome the undesirable rewetting and water absorption characteristic imparted by these treatments. In many cases the result is sub-standard. Known attempts to overcome this problem include the use of a fatliquor containing a polybasic acid ester (U.S. Patent 2,950,950) and the use of a fatliquor containing an alkyl phosphate (U.S. Patent 3,010,780). More recently, complete fatliquor systems incorporating alkyl phosphates as emulsifiers for leather oils have

been developed to overcome the deficiencies of the above approaches. All of the above systems are effective in lubricating leather, but do not supply a sufficient degree of internal water resistance unless used in excess. In order to achieve increased internal water resistance with the above systems, sufficient fatliquor must be added to penetrate the leather deeply, resulting in poor leather character and quality.

This invention makes it possible to gain internal water resistance and maintain good leather quality, relying less on the penetration of fatliquor for its effect. This system replaces or supplements conventional retan materials, thus improving the potential of all subsequent water repellant systems. This invention, while providing better internal water resistance, also provides retan effects. These effects are achieved by the use of leather treating compositions which comprise a phenol-polyphenol-aldehyde condensate subsequently alkoxylated and phosphated, as specified below. These compositions may be utilized for leather processing, and specifically for: retanning, lubricating effects such as softening and, primarily, for imparting water resistance to chrome and/or mineral tanned leather. Additionally, these compositions may be used to effect modifications of base mineral tannages for the purpose of dyeing, bleaching, and fatliquoring leather.

The expression "phenol" in this context means a substituted phenol or thiophenol having at least one hydrocarbon or substituted hydrocarbon substituent group selected from saturated or unsaturated; primary, secondary or tertiary; branched or straight-chain aliphatic radicals containing up to 20 carbon atoms. The expression "polyphenol" in this context means a polyhydric phenol, i.e. an aromatic hydrocarbon carrying at least two phenolic —OH groups.

According to the present invention, a leather treating composition is provided, comprising a phenol - polyphenol - aldehyde condensate which has been alkoxyated and phosphated, and in which:

- (A) the phenol is a substituted phenol or thiophenol having at least one hydrocarbon substituent group as hereinbefore defined,
- (B) the substituted phenol or thiophenol has or does not have at least one other substituent group,
- (C) the polyphenol is at least one polyphenol or substituted polyphenol, having from 2 to 15 benzene rings per molecule,
- (D) the phenol and the polyphenol are joined by at least one group derived from an aldehyde, substituted aldehyde, or aldehyde-liberating composition,
- (E) the alkoxyating agent has been reacted with the phenol-polyphenol-aldehyde condensate in the ratio of from 1 to 20 moles of alkoxyating agent per hydroxy group of the condensate, and
- (F) the phosphating agent has been reacted with the alkoxyated phenol-polyphenol-aldehyde condensate in the ratio of 0.25 to 4 moles of phosphating agent per hydroxy group of the alkoxyated condensate, the total number of benzene rings contained in one molecule of the condensate being from 3 to 16.

A method of treating leather, according to this invention, comprises contacting leather stock with a composition as defined in the preceding paragraph.

The general procedure for manufacturing the leather treating composition of this invention and the parameters of the ingredients thereof are as follows. Broadly, the procedure consists of condensing a phenol (as herein defined) and a polyphenol (as herein defined) with an aldehyde in the presence of an acid catalyst, neutralizing the catalyst with a strong base, alkoxyating the resulting polymer and phosphating the polymer in solution. Although phosphation of phenols directly is possible, it was considered better to facilitate the reaction by first alkoxyating the phenols.

The one or more hydrocarbon or substituted hydrocarbon substituent groups essentially required by the phenol contain up to 20 carbon atoms and are saturated or unsaturated; primary, secondary or tertiary; and branched or straight-chain; more than one such substituent group may be present in a phenol. Examples of useful substituent groups include, but are not limited to: dimethyl, ethyl, *n*-propyl, isopropyl, *sec*-butyl, *tert*-butyl, methylethyl, nonyl, decyl, dodecyl, pentadecyl, heptadecyl, eicosyl, diethylnonyl, hydroxymethyldodecyl and dimethyltetradecyl. Preferred substituent groups include alkyl groups which contain 6 to 18 carbon atoms and which are linear or branched chains. The hydrocarbon or sub-

stituted hydrocarbon substituent group or groups may be attached to any phenol or substituted phenol, examples of which include, but are not limited to: monohydric, dihydric and trihydric phenols; meta, ortho and para phenols; and more specifically: hydroxybenzene, cresol, xylene, chlorophenol, nitrophenol, 2,4-dinitrophenol, 1,3,5-trinitrophenol, 2 - isopropyl - 5 - methylphenol, 2 - methyl - 5 - isopropylphenol, *o* - dihydroxybenzene, *m* - dihydroxybenzene, *m* - dihydroxybenzene, *p* - dihydroxybenzene, 1-methyl-3,5-dihydroxybenzene, 1,2,3-trihydroxybenzene, 2,4,6-trihydroxybenzene, 1,2,4-trihydroxybenzene, fused ring phenols such as alpha-naphthol and beta-naphthol, pentachlorophenol, 2,4,6-tribromophenol, *p*-nitrosophenol, *o*-allylphenol, *p*-aminophenol and thiophenol. The preferred phenols are hydroxybenzene and naphthols.

Useful polyphenols include all of the above-mentioned phenols and substituted phenols multiplied so that there are from 2 to 15 benzene rings, as well as mixtures of the above phenols and substituted phenols combined so that there are from 2 to 15 benzene rings. Preferred polyphenols include: (dihydroxyphenyl) - benzene; 2,2 - bis(*p*-hydroxyphenyl) - propane; 1,1 - bis(*p*-hydroxyphenyl)-ethane; and bis-(hydroxybenzene).

The aldehydes are defined as aldehydes, substituted aldehydes, and aldehyde liberating compositions. Examples of useful aldehydes include, but are not limited to: formaldehyde, paraformaldehyde, trioxane, hexamethylenetetramine, formalin, acetaldehyde, propionaldehyde, butyraldehyde, heptaldehyde, furfuraldehyde, chloral, alpha-ethyl-beta-propylacrolein, benzaldehyde, glyoxal, pyruvaldehyde, cinnamaldehyde, pyrocatechualdehyde, veratraldehyde, crotonaldehyde, diphenylacetaldehyde, 2-ethylisovaleraldehyde, glutaraldehyde, mucobromic acid, *o*-anisaldehyde, 9-anthraldehyde, bromobenzaldehyde, carboxybenzaldehyde, cyanobenzaldehyde, dibenzoyloxybenzaldehyde, dibromosalicylaldehyde, dialdehyde starch, fluoronitrobenzaldehyde, indancarboxaldehyde, iodovanillin, isophthalaldehyde, mesitaldehyde, naphthaldehyde, nitropiperanol, syringaldehyde, tolualdehyde, bromoindolecarboxaldehyde, convallatozin, cymarin, ferrocenecarboxaldehyde, helveticoside, methylfurfuraldehyde, methylthiophenecarboxaldehyde, norbornenecarboxaldehyde and K-strophanthin. The preferred aldehydes or aldehyde-liberating compositions are formaldehyde, paraformaldehyde, trioxane, hexamethylenetetramine, formalin, acetaldehyde, propionaldehyde and butyraldehyde.

Useful phosphating agents include, but are not limited to: polyphosphoric acid, phosphorus pentoxide, pyrophosphoric acid, phosphoric acid, phospholeum (superphosphoric acid, phosphorus acid and phosphorus oxy-

chloride. Preferred phosphating agents are polyphosphoric acid, phosphorus pentoxide and phosphoric acid.

5 The desired proportions of phenol to polyphenol to aldehyde can best be shown by the following table, which represents the various ingredients and their proportions in terms of numbers of benzene rings. Thus, for example, the "optimal ratio" represents a tetraphenol  
10 consisting of 2 phenols, each joined by 1 aldehyde, to 1 diphenol. Another example would be a 15 ring polyphenol to which is joined 1 phenol by 1 aldehyde. Still another

example would be a diphenol to which is joined 14 phenols by 14 aldehydes. Thus, if  
15 it were desired to produce a polymer having 8 benzene rings, one could use 1 mole of phenol with 1 mole of a 7 ring polyphenol and 1 mole of aldehyde; or 2 moles of phenol  
20 with 1 mole of a six ring polyphenol and 2 moles of aldehyde; or 3 moles of phenol with 1 mole of a 5 ring polyphenol and 3 moles of aldehyde. The maximum total number of rings on the completed polymer which can  
25 be achieved in practice is indicated by the column on the extreme right.

| Ratio             | phenol | polyphenol | aldehyde | Maximum total rings |
|-------------------|--------|------------|----------|---------------------|
| lowest            | 1      | 2          | 1        | 3                   |
| optimal           | 2      | 2          | 2        | 4                   |
| highest preferred | 6      | 7          | 6        | 8                   |
| highest           | 14     | 15         | 14       | 16                  |

30 More specifically, phenol as described previously and a polyphenol as described previously are charged into a vessel and blended at a temperature of from about 25° to about 150°C and preferably 80° to 120°C. While  
35 blending, agitation is continued and an acid catalyst, in an amount of 0.1 to about 1%, by weight of the phenol-polyphenol mixture, is slowly added to the mixture. This catalyst may be any strong inorganic acid which will not react with an aromatic ring. Suitable  
40 acids include sulfuric acid, the halogen acids and substituted halogen acids. A particularly useful acid is hydrochloric acid. Phosphoro- and nitro-acids are not suitable. It is important at this stage to provide for removal of acid fumes formed by the high temperature  
45 of the mixture. If excessive acid catalyst is lost due to evaporation, more can be added within the above indicated amounts. The mixture is then heated to about 50° to about 150°C and preferably about 90° to about  
50 130°C and an aldehyde as described previously is added to the mixture slowly over a period of about 2 to about 6 hours, so that the temperature of the mixture is maintained at about 50° to about 150°C and preferably  
55 at about 90° to about 140°C. After the aldehyde has all been added, the mixture is then further reacted at about 60° to about 150°C and preferably about 100° to about 140°C for about 1 to about 5 hours. A strong  
60 base is then added slowly in a sufficient quantity to completely neutralize the acid. The salt thus formed is inert and may either be

removed or allowed to remain in the composition. Additional strong base is then added  
65 to make the resulting polymer mixture alkaline and facilitate alkoxylation. This base may be any inorganic alkaline substance which will not react with an aromatic ring and may advantageously be selected from sodium hydroxide, calcium hydroxide, magnesium  
70 hydroxide, potassium hydroxide and alkaline oxides. The polymer, which until this time has been prepared under a nitrogen blanket, is then stripped of the water which is a by-product of the reaction with a vacuum source  
75 capable of pulling from about 26 to about 32 inches of mercury and is held at this reduced pressure for about 15 to about 60 minutes until less than 0.1% water remains. The vacuum is then broken with a nitrogen  
80 blanket and the mixture is heated to about 100° to about 160°C and preferably about 115° to about 145°C. The polymer is then alkoxyated by adding an alkoxyating agent. Examples of useful alkoxyating agents include, but are not limited to ethylene oxide,  
85 propylene oxide, butylene oxide, isobutylene oxide and mixtures thereof. The preferred alkoxyating agent is ethylene oxide. The alkoxyating agent is added to the polymer in the ratio of about 1 to about 20 moles and preferably about 1 to about 3 moles, per  
90 hydroxy group of the polymer. The alkoxylation is desirably carried out at a temperature of about 100° to about 200°C, preferably at about 120° to about 160°C, and at a pressure of about 10 to about 30 p.s.i.g. Solvent

- is then added to adjust the solids content of this composition to about 70% by weight for ease of handling. This polymer is selectively soluble in aromatic solvents, such as toluene, chlorobenzene and xylene, and substituted chlorinated hydrocarbons, such as ethylene dichloride. The preferred solvent is xylene. The composition thus produced is an intermediate polymer solution comprising an alkoxylated phenol - polyphenol - aldehyde condensate.
- The leather treating composition is then prepared as follows. The intermediate polymer solution containing 70% solids by weight prepared as described above is charged into a vessel and heated to about 50° to about 70°C. The phosphating agent is then added in the ratio of about 0.25 to about 4 moles and preferably about 1 to about 2.5 moles per hydroxyl group on the polymer. The phosphating agent, which is selected from among those described previously, is added slowly while maintaining the temperature at about 50° to about 80°C. The mixture is then heated to about 60° to about 150°C and preferably about 80° to about 110°C and maintained at this temperature for about 1½ to about 2½ hours, until phosphation is completed. A mixture of water and a strong base is then slowly added to adjust the composition to a neutral pH. The strong base may be selected from among any of those given above. Finally, additional water is added sufficient to adjust the solids content of the mixture to about 35 to about 40% by weight.

### EXAMPLE I

An intermediate polymer was prepared using the following ingredients:

| Ingredient |   | Parts by Weight |
|------------|---|-----------------|
| (A)        | octyl-phenol                              | 30.03           |
| (B)        | 2,2-bis-( <i>p</i> -hydroxyphenyl)propane | 16.59           |
| (C)        | paraformaldehyde flakes                   | 4.56            |
| (D)        | hydrochloric acid, 20° Bé                 | 0.75            |
| (E)        | potash caustic liquid, 45%                | 1.08            |
|            |   | 53.01           |
| (F)        | waste*                                    | -3.41           |
|            |   | 49.60           |
| (G)        | ethylene oxide                            | 19.71           |
| (H)        | xylene, commercial                        | 30.69           |
|            |   | 100.00          |

\* waste material consists of water plus traces of HCl, formaldehyde, octyl-phenol, and 2,2-bis-(*p*-hydroxyphenyl)-propane fumes.

- The preparation of this polymer was as follows. This reaction was carried out under a nitrogen blanket when not in vacuo. Ingredients (A) and (B) were charged into a glass-lined reactor. The mixture was heated to 95°C and thoroughly blended with a variable speed agitator. While agitation was continued, ingredient (D) was slowly added over a period of 15 minutes. Provision was made for adequate ventilation to remove acid fumes generated during this step. The mixture was then heated to 105°C and ingredient (C) was added in 20 equal increments over a period of 3 to 4 hours, so that the temperature of the mixture was maintained at 105°C to 110°C. The mixture was then reacted at 120±5°C for 3 hours to form a polymer. Ingredient (E) was then added slowly over a 30 minute period. The polymer was then stripped of water with a vacuum source capable of pulling 28 inches of mercury and held at reduced pressure for 30 minutes. The

vacuum was then broken with a nitrogen ture was raised to  $140 \pm 10^\circ\text{C}$  at 25 p.s.i.g. 5  
blanket. and the mixture was reacted for 30 minutes.

The mixture was then heated to  $130^\circ\text{C}$ . Ingredient (H) was then added to adjust the  
and ingredient (G) was added. The tempera- solids content to about 70%.

## EXAMPLE II

A leather treating composition was prepared using the following ingredients:

| Ingredient                     | Parts by Weight |
|--------------------------------|-----------------|
| (A) product of Example 1       | 35.40           |
| (B) polyphosphoric acid        | 8.26            |
| (C) potash caustic, 45% liquid | 17.57           |
| (D) water                      | 38.77           |

10 The preparation of this composition was  
as follows. Ingredient (A) was charged into a  
glass-lined reactor and heated to  $60^\circ\text{C}$ . In-  
15 ingredient (B) was then slowly added over a  
period of 2 to 3 hours, while maintaining the  
temperature at  $60^\circ\text{--}70^\circ\text{C}$ . The mixture was  
heated to  $95 \pm 5^\circ\text{C}$  and maintained at this  
temperature for 2 hours. The mixture was  
20 then cooled to less than  $30^\circ\text{C}$ . A premix of  
ingredients (C) and (D) was slowly added over  
a 2 hour period, while keeping the temper-  
ature of the mixture at less than  $40^\circ\text{C}$ . Addi-  
tional amounts of ingredient (C) were then  
25 added to adjust the pH of a 5% solution to  
about 7. Finally, additional amounts of in-  
ingredient (D) were added to adjust the solids  
content of the mixture to about 37%. The  
composition thus produced was an effective  
leather treating composition within the scope  
of this invention.

## EXAMPLE III.

30 Application tests were conducted of pro-  
ducts prepared in the manner of Example II,  
but phosphated to (4) 50% and (5) 75% res-  
pectively as compared with (3) an alkyl di-  
35 phenyl phosphate, (2) a substituted phenolic  
sulfonate, and (1) a chrome control in which  
there was no retannage. The tests were con-  
ducted in the following manner.

The leather used was Trostel stock 5—5½  
40 oz. grains. All percentages are based on the  
wrung split shave weight as received, which  
is normally 40 to 50% water. The application  
procedure was as follows:

- 45 (1) The stock was washed in 400% water  
for 15 minutes and drained. This re-  
moved the majority of the loose  
chrome salts and acids.  
(2) The stock was refloatated in 100%  
water at  $80^\circ\text{F}$  and neutralized with

the following percentages of sodium 50  
bicarbonate and run for 30 minutes.

- Test 1 0.75% sodium bicarbonate  
Test 2 0.50% sodium bicarbonate  
Test 3 0.06% sodium bicarbonate  
Test 4 0.06% sodium bicarbonate 55  
Test 5 0.06% sodium bicarbonate

The percentage of sodium bicarbonate  
was reduced for Tests 3—5 to com-  
pensate for the alkali content of  
60 samples.

- (3) The stock was washed in a float at  
130°F for 10 minutes and drained, in  
order to remove remaining chrome  
salts as well as salts resulting from the  
neutralization step. 65  
(4) About 2 to 10% solids of the syntans  
to be tested per 100% water were  
added at 130°F and run for 1—1½  
hours.  
(5) The systems were adjusted with formic 70  
acid to the lowest equilibrium pH and  
were run for 15 minutes.  
(6) The systems were adjusted with formic  
acid to a pH of 3.5 and run an addi-  
tional 15 minutes. 75  
(7) The stock was washed for 10 minutes  
in cold water and mid-bend pieces  
were removed for non-fat observation.  
(8) The stock was heated to 130°F,  
washed for 10 minutes and drained. 80  
(9) The remaining pieces of stock were  
fatliquored with 8% solids per 100%  
float at 130°F. The fatliquor used was  
an emulsified oil, whose emulsifier is  
85 of a non-rewetting character.  
(10) The stock was rinsed, washed for 10  
minutes and horsed up.  
(11) The stock was wrung out and tacked  
up to dry in an oven at 140°F for  
90 four hours.

- (12) The stock was allowed to lay over for three days to pick up moisture.  
 (13) The stock was dried staked and tested for temper, water resistance, grain strength and light fastness.

#### EXAMPLE IV.

The results of testing of the five stocks prepared in Example III were as follows. The stocks were subjected to a standard Maeser flex test with the following results.

10

#### STOCK

|  | 1*  | 2* | 3*   | 4*  | 5*  |
|--|-----|----|------|-----|-----|
| A. Tests with fat liquor (Step 9) omitted  |     |    |      |     |     |
| No. of flexes for initial water penetration                                      | 52  | 40 | 1020 | 234 | 200 |
| cc of water transmitted in 8,000 flexes  | 9   | 19 | 4    | 33  | 22  |
| Percentage of water compared to initial weight of stock absorbed in 8,000 flexes | 100 | 99 | 23   | 51  | 35  |

#### STOCK

|  | 1*  | 2*  | 3*   | 4*  | 5*  |
|--|-----|-----|------|-----|-----|
| B. Tests with fat liquor (Step 9) included                                       |     |     |      |     |     |
| No. of flexes for initial water penetration                                      | 510 | 340 | 4000 | 285 | 611 |
| cc of water transmitted in 8,000 flexes  | 13  | 32  | 0.2  | 48  | 11  |
| Percentage of water compared to initial weight of stock absorbed in 8,000 flexes | 55  | 56  | 12   | 25  | 10  |

- \*1 Control stock — no retannage (step 4).  
 \*2 Syntan was a substituted phenolic sulfonate (50% solids) which is a conventional type.  
 \*3 Syntan was an ethoxylated alkyl diphenyl phosphate (72% solids).  
 \*4 Syntan was an ethoxylated phenol-bisphenol-aldehyde condensate which was 50% phosphated (80% solids) and which falls within the scope of this invention.  
 \*5 Syntan was an ethoxylated phenol-bisphenol-aldehyde condensate which was 75% phosphated (80% solids) and which falls within the scope of this invention.

15 The most important data relate to the percentage of water absorbed by the stock. Low water absorption is preferred and such a quality is indicated by a lower number. Although Stock No 3 had the best water

absorption resistance, this stock was completely unsatisfactory because of its poor esthetic qualities, namely, excessively coarse and loose break. Stocks Nos. 4 and 5, which were within the scope of this invention, were clearly sup-

20

erior to Stock No. 1 which used no syntan and to Stock No. 2 which used a conventional syntan.

A test was then conducted to determine

the temper of fatted and nonfatted stock using a Stubbings Temper Machine (Milwaukee School of Engineering). The results of this test are as follows.

### STOCK

| 1  | 2  | 3  | 4  | 5  |
|--|----|----|----|----|
| A. Tests with fat liquor (Step 9) omitted  |    |    |    |    |
| 24   | 44 | 70 | 58 | 60 |
| B. Tests with fat liquor (Step 9) included |    |    |    |    |
| 44   | 60 | 79 | 68 | 77 |

10 A higher number in this test represents a softer leather and conversely a lower number represents a firmer leather.

Both water resistance and lubrication effects are realized by the use of the composition of the subject invention on Trostel cowhide grains. A definite ability to open up cowhide structure is demonstrated, this being a characteristic which very few materials at low levels of application can accomplish. Retan effects such as a more unique and lighter chrome color and reduction of surface stock harshness are realized, but a filling of the leather does not occur despite the plumpness and resinous feel imparted to it in the wet condition. The plumpness and feel are apparently related to the opening up and hydrophobicity characteristics imparted by these systems. Low level applications for such uses as shoe uppers, gloves and garments are useful and the compositions may be used with any type of leather, for instance deer skin or cow splits.

#### WHAT WE CLAIM IS:—

35 1. A leather treating composition, comprising a phenol-polyphenol-aldehyde condensate which has been alkoxyated and phosphated, and in which:

40 (A) the phenol is a substituted phenol or thiophenol having at least one hydrocarbon substituent group as hereinbefore defined.

(B) the substituted phenol or thiophenol has or does not have at least one other substituent group.

45 (C) the polyphenol is at least one polyphenol or substituted polyphenol, having from 2 to 15 benzene rings per molecule,

(D) the phenol and the polyphenol are joined by at least one group derived from an aldehyde, substituted aldehyde, or aldehyde-liberating composition,

50 (E) the alkoxyating agent has been reacted with the phenol-polyphenol-aldehyde condensate in the ratio of from 1 to 20 moles of

alkoxyating agent per hydroxy group of the condensate, and

(F) the phosphating agent has been reacted with the alkoxyated phenol-polyphenol-aldehyde condensate in the ratio of 0.25 to 4 moles of phosphating agent per hydroxy group of the alkoxyated condensate, the total number of benzene rings contained in one molecule of the condensate being from 3 to 16.

2. A composition according to claim 1, in which the substituent group of the phenol (A) is a C<sub>6</sub> to C<sub>18</sub> alkyl group.

3. A composition according to claim 1 or 2, in which (B) is one or more hydroxybenzene, alpha-naphthol and beta-naphthol, carrying the at least one hydrocarbon substituent group of (A).

4. A composition according to any preceding claim, in which the phenol is octylphenol.

5. A composition according to any preceding claim, in which the polyphenol (C) is one or more of (dihydroxyphenyl)-benzene, bis - (hydroxybenzene) 2,2 - bis(*p* - hydroxyphenyl) - propane and 1,1 - bis(*p* - hydroxyphenyl) - ethane.

6. A composition according to any preceding claim, in which the total number of benzene rings in the polyphenol is not less than 2 nor more than 15 and in which not less than 1 nor more than 14 moles of aldehyde are used to join not less than 1 nor more than 14 phenols to the polyphenol.

7. A composition according to claim 6, in which the polyphenol has not more than 7 benzene rings and in which not more than 6 phenols are joined to the polyphenol, connected by not more than 6 moles of aldehyde.

8. A composition according to claim 7, in which a polyphenol having 2 benzene rings is condensed with 2 phenols by means of 2 moles of aldehyde.

9. A composition according to any pre-

- ceding claim in which (D) is one or more of formaldehyde, paraformaldehyde, trioxane, hexamethylene-tetramine, formalin, acetaldehyde, propionaldehyde and butyraldehyde.
- 5 10. A composition according to any preceding claim, in which the alkoxylating agent is one or more of ethylene oxide, propylene oxide, butylene oxide and isobutylene oxide.
- 10 11. A composition according to any preceding claim, in which the alkoxylating agent is reacted with the phenol-polyphenol-aldehyde condensate in the ratio of from 1 to 3 moles of alkoxylating agent per hydroxy group of the condensate.
- 15 12. A composition according to any preceding claim, in which the phosphating agent is one or more of polyphosphoric acid, phosphoric acid, phosphorous pentoxide, pyrophosphoric acid, phosphorous acid, phospholeum and phosphorous oxychloride.
- 20 13. A composition according to any preceding claim, in which the phosphating agent is reacted with the alkoxylated phenol-polyphenol-aldehyde condensate in the ratio of 1 to 2.5 moles of phosphating agent per hydroxy group of the alkoxylated condensate.
- 25 14. A composition according to claim 1, substantially as herein described.
- 30 15. A method of treating leather which comprises contacting leather stock with a composition as defined in any preceding claim.
- 35 16. Leather when treated by a method according to claim 15.
17. A method of treating leather stock whose wrung split shave weight is normally 40% to 50% by weight of water, which comprises:
- 40 (A) washing the stock in 400% water for 15 minutes and draining,
- (B) refloating the stock for 30 minutes in 100% water at 80°F. and neutralizing with 0.06% sodium bicarbonate,
- (C) washing the stock in a float at 130°F. for 10 minutes and draining,
- (D) adding 2% to 10% by weight of solids of a leather treating composition (syntan) per 100% water at 130°F. and running for 1½ hours,
- (E) adjusting the system with formic acid to the lowest equilibrium pH and running for 15 minutes,
- (F) further adjusting the system with formic acid to a pH of 3.5 and running for an additional 15 minutes.
- (G) washing the stock for 10 minutes in cold water,
- (H) heating the stock to 130°F., washing for 10 minutes and draining,
- (I) fat-liquoring the stock with 8% solids per 100% float at 130°F. with a fat liquor consisting of an emulsified oil whose emulsifier is of a non-rewetting character,
- (J) rinsing the stock, washing for 10 minutes and horsing up the stock,
- (K) rinsing out the stock and tacking it up to dry in an oven at 140°F. for 4 hours,
- (L) allowing the stock to lay over for 3 days to pick up moisture, and
- (M) drying and staking the stock,
- wherein the leather treating composition used in step D comprises a phenol-polyphenol-aldehyde condensate according to any of claims 1 to 14.
- POLLAK, MERCER & TENCH,  
Chartered Patent Agents,  
Audrey House, Ely Place,  
London, EC1N 6SN,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.